

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

NO DRAWINGS

Process for the Recovery of ϵ -Caprolactam From Polycaprolactams

We, ALLIED CHEMICAL CORPORATION, a Corporation organised and existing under the laws of the State of New York, United States of America, of 61 Broadway, New York 6, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a process for the recovery of epsilon-caprolactam from polycaprolactam.

Synthetic linear polyamides derived from ϵ -caprolactam, generally known as nylon 6 polymers are used in the manufacture of fibres, films, moulded articles and other useful products. The manufacture of polymer products frequently involves the accumulation of considerable amounts of waste polymer material. In view of the cost of manufacture of these polyamides, the economic recovery of the monomeric intermediate, ϵ -caprolactam, in a form capable of undergoing repolymerization is of great importance.

The recovery of ϵ -caprolactam from its polymers is generally effected by an operation referred to as depolymerization. Various specific depolymerization processes have been proposed, the most important being those involving the combined action of steam and orthophosphoric acid on molten polymer in which ϵ -caprolactam is obtained mixed with water as an effluent condensate. The phosphoric acid (H_3PO_4) is believed to function as a catalyst for the depolymerization, but has generally been required in large amounts, likely to cause or accentuate corrosion, and its use has led to low efficiencies of ϵ -caprolactam recovery rates, and low concentrations of monomer in the

aqueous condensate produced. Continuous operation of depolymerization systems has thus been unsuccessful because of the large amounts of residual, non-depolymerizable material which accumulates, and the non-uniform reaction rates. Because ϵ -caprolactam and water form eutectic mixtures, it is generally expensive commercially to recover by crystallization or distillation ϵ -caprolactam from aqueous condensates containing less than a 35% concentration thereof.

The present invention provides a continuous process for the efficient recovery of ϵ -caprolactam from polycaprolactams, under conditions which minimize corrosive damage to the metal equipment employed in the process. The ϵ -caprolactam is recovered as a concentrated aqueous solution from which it can be efficiently isolated in a form suitable for re-polymerization to form polyamides.

The process of the invention comprises continuously feeding polycaprolactam and orthophosphoric acid in the proportion of 0.1 to 5 parts by weight of the latter (calculated as 100% acid) to 100 parts by weight of the former to a depolymerization zone, in which they are kept at a temperature of 220°-375°C. and at a pressure of 0.5 to 6 atmospheres absolute, continuously feeding steam into the said zone, and continuous withdrawing a mixture of steam and ϵ -caprolactam vapour therefrom, the rate of feed of the steam, polymer, and orthophosphoric acid being such that the mixture withdrawn contains not more than 80% by weight of ϵ -caprolactam, and that the volume of reactants in the said zone remains substantially constant. The new process is said to be continuous in the sense that the amount of material fed to the depolymerization zone during a single run

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is at least five times the volume of the said zone.

It has been found that phosphoric acid when introduced in rather low proportions with polycaprolactam into a depolymerization zone, rapidly loses its catalytic activity during the depolymerization process. Introducing larger proportions of the phosphoric acid serves to maintain the catalytic action, but leads to the formation of non-recoverable residues, to production of lactam in only low concentration, and to possible corrosive damage to the metal of the reaction vessel. The present invention is based on the surprising discovery that by continuously introducing into the depolymerization zone phosphoric acid and polymer in a ratio of acid:polymer maintained below a critical maximum, and adding fresh phosphoric acid and polymer in like proportions at a regulated uniform rate to the system, and maintaining other process parameters within definite ranges, a highly efficient continuous process may be operated.

In the new process the feed rate of steam, polymer and phosphoric acid is adjusted in relation to temperature, pressure, and steam flow rate to maintain the reactants at a substantially constant volume as this has been found to be important for continuous operation with consistently high efficiency. Similarly the reactants are maintained at approximately constant temperature and act as a solvent and moderating agent. The polymer and orthophosphoric acid may be fed to the depolymerization zone as a mixture prepared by mixing polycaprolactam with orthophosphoric acid, water and ϵ -caprolactam, and heating the mixture at a temperature of 160°C. to 250°C. for one to four hours under autogenous pressure of 5-14 atmospheres. The heating of the mixture may be accomplished by contact with high pressure steam, radiant heating, indirect heat exchange, or other methods. The presence of the phosphoric acid during the formation of the solution of polymer has been found to afford the unexpected advantage of lowering the viscosity of the solution. It is convenient and efficient to supply the polymer as a solution in ϵ -caprolactam, although this is not essential. Once formed, the solution of the polymer is preferably added as a continuous stream to the depolymerization zone at a volumetric rate such that a substantially constant volume is maintained in the depolymerization zone.

The depolymerization process of the invention may be carried out in equipment such as kettles provided with fluid inlet and outlets, means for agitating the fluid contents of the vessel, steam inlet, means for the removal of overhead vapours, heating means, and means for improving gas-liquid interfacial contact. It is preferable to em-

ploy heating means which, by radiation or thermal conduction, supply at least 40% of the heat to the depolymerization zone, the remainder of the heat in said zone being supplied by the steam throughput. Ordinary materials of construction may be employed in view of the relatively non-corrosive nature of the operation. Detection and control devices may be suitably employed to maintain desired temperatures, agitation rates, and steam flow rates.

The temperature of the reactants is between 220°C. and 375°C. and should be held approximately constant to obtain consistently efficient operation. The pool of reactants in the depolymerization zone can be formed by accumulating the reaction mixture, e.g. by feeding the phosphoric acid/polymer mixture to the said zone under the conditions of the new process except that the steam input rate is low; or the pool can be formed under conditions other than those in the new process, e.g. using larger amounts of phosphoric acid than those specified.

The phosphoric acid, although preferably added to the depolymerization zone mixed with a solution of the polymer, may however be added separately. It may be added in requisite amounts continuously to the depolymerization zone, or may be added in discrete batchwise additions of uniform regularity. It is essential however that the phosphoric acid be added to the depolymerization zone during the operation of the process in amounts averaging between about 0.1 parts and 5 parts per 100 parts by weight of polymer introduced. Preferably the phosphoric acid is added in proportions averaging between about 0.1 and 1 part per 100 parts of polymer and not exceeding at any time during the continuous operation 3 parts per 100 parts of polymer.

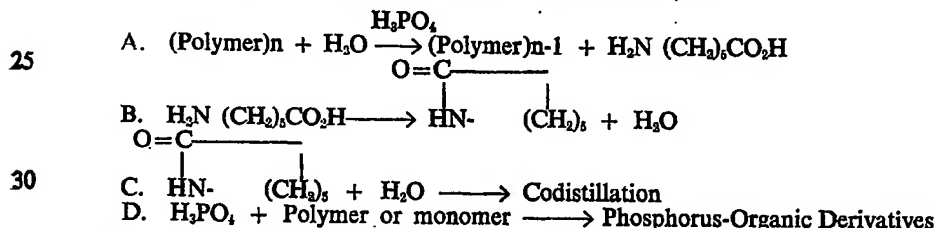
Chemical analysis of the depolymerizing mixture indicates that under the conditions of the new process the orthophosphoric acid is converted at a substantially steady rate into complex phosphorus-organic derivatives which are ineffective as catalysts and represent a loss of recoverable monomer. If larger amounts of phosphoric acid than 5 parts per 100 parts of polymer are introduced in the depolymerization mixture, the formation of such phosphorus-organic derivatives is greatly accelerated, resulting in losses of phosphoric acid and lactam, and formation of tars imparting excessively high viscosities to the pool of reactants, inhibiting further continuous operation. However, under the conditions defined above, the new process gives conversion efficiencies better than 90%; that is, more than 90% of the theoretically recoverable lactam is obtained, based on the amount of polycaprolactam introduced into the depolymeri-

zation zone.

The steam employed may be either saturated or super-heated. It is generally introduced into the bottom of the depolymerization zone through a sparger or analogous device with facilitates efficient contact of the steam with the depolymerizing mixture, and provides agitation of the mixture. Although the steam delivers some heat to the depolymerization zone, its principal function is to carry the produced lactam

out of the depolymerization zone to a condenser and recovery zone. In accomplishing these objectives most effectively, the rate of steam employed is preferably between 0.25 to 1.5 parts by weight of steam per part by weight of polymer feed.

In the course of the depolymerization reaction, a complex series of physical and chemical changes recur some of which may be approximately represented by the following equations:



Reaction A is dependent upon temperature, phosphoric acid concentration, water concentration and amino-acid concentration. Reaction B is dependent upon temperature and concentrations of water, amino acid, and lactam. Occurrence C is dependent upon temperature, pressure, steam flow rate, viscosity of the mixture, and concentrations of water and lactam. Reaction D depends primarily upon the concentration of free orthophosphoric acid. Since the overall process is operated continuously under non-equilibrium conditions, the yield of lactam in the overhead condensate is affected more by the rates of the various occurrences (A) to (D) than by equilibrium considerations. It is thus seen that the limitations which define the surprisingly efficient process of this invention delineate unobvious critical conditions for the successful accomplishment of the desired objectives.

In view of the relatively insignificant corrosive action of the depolymerizing mixture compared with mixtures used in prior art methods of depolymerizing polycaprolactam it is not essential that glass-lined, or polymer-lined vessels be employed, nor is it essential to incorporate corrosion-inhibiting substances in the depolymerizing mixture. However, in the case of systems consisting of unlined ferrous vessels and auxiliary equipment, it may be desirable to incorporate corrosion inhibiting substances in the depolymerization mixture to prevent damage caused by accidental spillage of the concentrated phosphoric acid used in the process, or accidentally high concentrations of phosphoric acid in the depolymerization zone. Heavy metal ions, e.g. copper, manganese or tin ions, may be included in the depolymerizing mixture in amounts ranging from 20 parts per million to about 5% for such purpose, and do not interfere with the

depolymerization process.

By regulation of the proportional steam input and polymer quantities, the effluent vapour from the depolymerizing zone is preferably made to contain between 35% and 80% ϵ -caprolactam by weight. Effluent concentrations of ϵ -caprolactam below 35% create recovery problems; and, under conditions which provide concentrations above 80%, it is found that the rate of depolymerization becomes impracticably slow. On condensation of the effluent vapours, a homogeneous solution forms, from which the lactam is easily recoverable. For example, the water may be removed by conventional evaporation at normal or reduced pressures, by flash evaporation processes, membrane diffusion processes, azeotropic distillations, counter-current treatment with anhydrous inert gases, treatment with hydratable inorganic salts or active zeolites such as "molecular sieves", or non-contacting exposure to water-reactive compounds such as phosphorus pentoxide. It is generally not required that the caprolactam be recovered in completely anhydrous condition, since the reconversion of the caprolactam into useful polymer can generally be effected in the presence of water, e.g. as described in United States Patent No. 2,241,321. The caprolactam obtained by the process of this invention, after recovery from the aqueous condensate, will generally have a Permanganate Number below about 20, determined from optical density resulting from reaction with permanganate under standard test conditions outlined, e.g. in Specification No. 854,538; and an APHA colour below about No. 20 (Pt-Co standard, 100% basis). These are characteristics of good quality monomer suitable for repolymerization without further purification.

The new process gives rise to a small amount of non-volatile residue. Residual,

non-depolymerizable material may be periodically removed from the depolymerization vessel; or a small quantity of liquid can be periodically or continuously withdrawn from the vessel as a bleed for purposes of maintaining the tar accumulation below a selected maximum level.

While the invention essentially relates to the recovery of ϵ -caprolactam from polymer compositions consisting entirely of poly- ϵ -caprolactam homopolymer, it will be understood that the presence in the polymer compositions of a small proportion of polymer units derived, for example, from higher lactams or diamines and diacides will not adversely affect the efficacy of the process. Linear caprolactam polymers of any molecular weight are found satisfactorily amenable to the process of this invention, including oligomers consisting of only several monomeric units. The polymer composition may contain conventional additives such as fillers, pigments, flame retardants, anti-static agents, mould release agents, and plasticizers. It is preferred however that little if any volatile components be present.

The pressure within the depolymerization vessel may be controlled, for example, by the pressure of the inlet gas in conjunction with outlet gas valve; by raising the temperature of the gas confined in the depolymerization zone; or by mechanically compressing the gas in the said zone. Pressures below $\frac{1}{2}$ atmosphere, representing a partial vacuum, are inoperative because of the inadequate concentrations of water in the depolymerizing mixture. Pressures above 6 atmospheres generally provide diminished rates of lactam recovery, possibly because of adverse effects on the concentration and interphase relationships of the effluent vapour mixture of water and lactam.

The following Example describes a specific embodiment of the invention. All parts and percentages are by weight unless otherwise specified.

EXAMPLE

Into each of 2 separate vessels in turn was charged 1,000 pounds of polycaprolactam scrap in the form of ground-up solid waste, 2.25 pounds of aqueous 85% orthophosphoric acid, and 1,000 pounds of aqueous 50% ϵ -caprolactam solution. The vessels, thus charged, were sealed shut. Heated fluid at 175°C.-180°C. was passed through the external heating jacket. At the same time, high pressure steam at 175°C.-180°C. and about 125-130 p.s.i.g. was injected into the mixture in the vessel. The steam injection was discontinued when the batch temperature reached about 175°C. The contents of the vessel were held at about 175°C. under autogenous pressure of 123-135 p.s.i.g. for $\frac{1}{2}$ hour without agitation.

While the dissolved polymer mixture thus prepared was being fed from one dissolving vessel to a depolymerization vessel, additional solution was being prepared in the second dissolving vessel.

The polymer solution was continuously fed at a substantially uniform rate of 1,300 pounds per hour into a depolymerization vessel of 8,000 United States gallons capacity equipped with an external heating jacket, internal heating coils, and steam sparger, made of stainless steel. A pool of approximately 2,000 United States gallons of depolymerizing mixture was allowed to accumulate and was thereafter maintained in the kettle. The pool temperature was maintained at 275°C. Superheated steam at 350°C. and 100 p.s.i.g. entered the bottom of the pool through a sparger at the rate of 700 pounds per hour. At least about 40% of the heat supplied to the pool was supplied via the heating jacket and coils, the remainder being supplied by the steam. The pressure above the pool of depolymerizing mixture was about 3 to 6 p.s.i.g.

Vapours consisting of water and ϵ -caprolactam were continuously evolved from the depolymerization vessel at a substantially uniform rate of about 2,000 pounds of vapours per hour having an average lactam content of about 45-50% by weight.

The above described conditions of operation were maintained during a continuous throughput of 100,000 pounds of the polycaprolactam scrap.

For purposes of determining the amount of residue, the depolymerizing pool was then allowed to run dry by cutting off the feed stream of dissolved polymer mixture while continuing the steam flow. The residual product thus obtained, which afforded no further lactam upon continued application of steam, weighed about 2,000 pounds. The overall efficiency of recovery of monomer from the polycaprolactam feed stock was thus about 98%.

The residual product consisted of a complex mixture of high-melting cross-linked polymer and phosphorus-organic compounds. The residual product, although having a phosphorus content corresponding to about 7.5% by weight as orthophosphoric acid, contained less than 5% by weight of free orthophosphoric acid. This residue, although representing a loss insofar as recovery of ϵ -caprolactam monomer is concerned, can be converted into useful shaped solid or foamed objects which are flame-proof because of their high phosphorus content. Corrosive damage to the metal parts contacted by the depolymerizing mixture was negligible, as determined by 6 months continuous equipment operation.

BATCHWISE TEST RUNS

In order to determine the effect of the

proportion of orthophosphoric acid introduced on the depolymerization process of this invention, a series of test runs was performed under varying conditions of operation using batchwise charges of known composition in the depolymerization vessel.

The data showing conditions and results are presented in Table I. "Recovered Lactam Concentration" expresses concentration of lactam (weight percent) in the condensed

vapours; and " H_3PO_4 (%)" expresses weight percent of commercial aqueous 85% phosphoric acid in the batch of acid and polycaprolactam introduced into the reaction vessel. Runs, A, B, and C are tests of conditions within the range used in our process, whereas runs D, E, F, and G employ certain conditions outside the ranges used in our process.

Table I

Process Variable	A	B	C	D	E	F	G
Recovered Lactam Concentration	55%	55%	55%	37%	10%	85%	39%
Steam Rate, (grams/hour)	300	360	720	500	720	100	300
Temperature of the Steam ($^{\circ}\text{C}.$)	400	400	400	400	300	400	280
Polymer Pool Temperature ($^{\circ}\text{C}.$)	360	340	320	300	300	370	210
H_3PO_4 (%)	1.8	2.4	3.0	7.0	16.7	2.3	3.3
Lactam Production Rate (grams/hour)	367	440	880	300	80	230	180
Heavy Metal (ppm)							
Cu	10		70		40		
Mn	20	20	50	70		30	60
Sn		10					
Overall Efficiency (%)	98	94	93	95	75	89	95

As the data of runs D, E, F and G of Table I indicate, conditions of temperature, recovered lactam concentration, or H_3PO_4 concentration outside the permissible range of process limitations of this invention result in unduly low overall efficiencies (below 90%) or unduly low rates of lactam production (below 350 grams per hour).

WHAT WE CLAIM IS:

1. A process for the recovery of ϵ -caprolactam from polycaprolactam which comprises continuously feeding the said polymer and orthophosphoric acid in the proportion of 0.1 to 5 parts by weight of the latter (calculated as 100% acid) to 100 parts by weight of the former to a depolymerization zone, in which they are kept at a temperature of 220° - $375^{\circ}\text{C}.$ and at a pressure of 0.5 to 6 atmospheres absolute, continuously feeding steam into the said zone, and continuous withdrawing a mixture of steam and ϵ -caprolactam vapour therefrom, the rate of feed of the steam, polymer, and orthophosphoric acid being such that the mixture withdrawn contains not more than 80% by weight of ϵ -caprolactam, and that the volume of reactants in the said zone remains substantially constant.

2. Process according to claim 1 in which the mixture withdrawn from the depolymerization zone contains 35 to 80% by weight of ϵ -caprolactam vapour.

3. Process according to claim 1 or 2 in which the polycaprolactam and orthophosphoric acid are fed to the depolymerization zone as a solution comprising the said polymer and acid dissolved in a mixture of water and ϵ -caprolactam.

4. Process according to any of claims 1 to 3 in which the proportion of orthophosphoric acid fed to the depolymerization zone averages 0.1 to 1 part by weight per 100 parts by weight of polycaprolactam fed to the said zone, and at no time exceeds 3 parts per said 100 parts.

5. Process according to any of claims 1 to 4 in which the reactants in the depolymerization zone contain from 20 parts per million to 5% of copper, manganese or tin.

6. Process according to any of claims 1 to 5 in which not more than 60% of the heat required to maintain the temperature of 220° - $375^{\circ}\text{C}.$ is supplied by the steam fed to the depolymerization zone.

7. Process according to claim 1 substantially as described in the Example.

8. ϵ -Caprolactam when produced by the process of any of the preceding claims.

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